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Synthetic Organic Chemicals

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Tackling Difficult Distillations

DISTILLATION under reduced pressure has become a commonplace operation for the purification of organic chemicals. Each laboratory has its own favored technique, but the principle involved remains the same. The liquid is contained in a flask connected to one or more condensers by relatively narrow tubes and stop cocks, and air or other gas is bubbled through during distillation to act as a carrier for the vapor.

There are many liquids so easily decomposable, or so involatile that the degree of evacuation possible with this apparatus is inadequate. If the stop cocks are greased, the grease contaminates the distillate; if they are left unlubricated, they leak. The tubes are generally too narrow to give quick transfer of the extremely tenuous vapor, while the liquid, if robbed of its current of air to produce the highest vacua, may bump explosively at its boiling point. These difficulties were suffered acutely in the Kodak Research Laboratories when distilling liquids which ordinarily decompose however carefully they are vaporized. A new technique which is described in a recent issue of the *Journal of the Optical Society of America* was developed and has recently been extended so that even such complex substances as castor oil may be distilled, or rather sublimed, without appreciable loss. This note is an account of the extension.

A substance will distill under most favorable conditions when:

(a) The pressure is low.

(b) The temperature is low.

(c) The distance between the surface of the liquid and the surface of the condenser is less than the mean free path of the molecules at the pressure in question.

(d) The path of the vapor is wide.

The last three items can readily be controlled during construction or manipulation. The first—low pressure—may be difficult of attainment because of:

1. Leaks.
2. Evolution of dissolved air from the liquid.
3. Presence of volatile impurities which have a vapor pressure slightly greater than that of the substance.
4. Decomposition during distillation with the evolution of:

(a) Non-condensable gases.

(b) Easily condensable materials.

Although leaks and dissolved air can be taken care of quite easily, impurities and cracking cause a lot of trouble. With the apparatus shown in the accompanying sketch all the troubles can be minimized or eliminated.

A very stout pyrex flask of 600-1000 cc. capacity is given a waist in the mid-

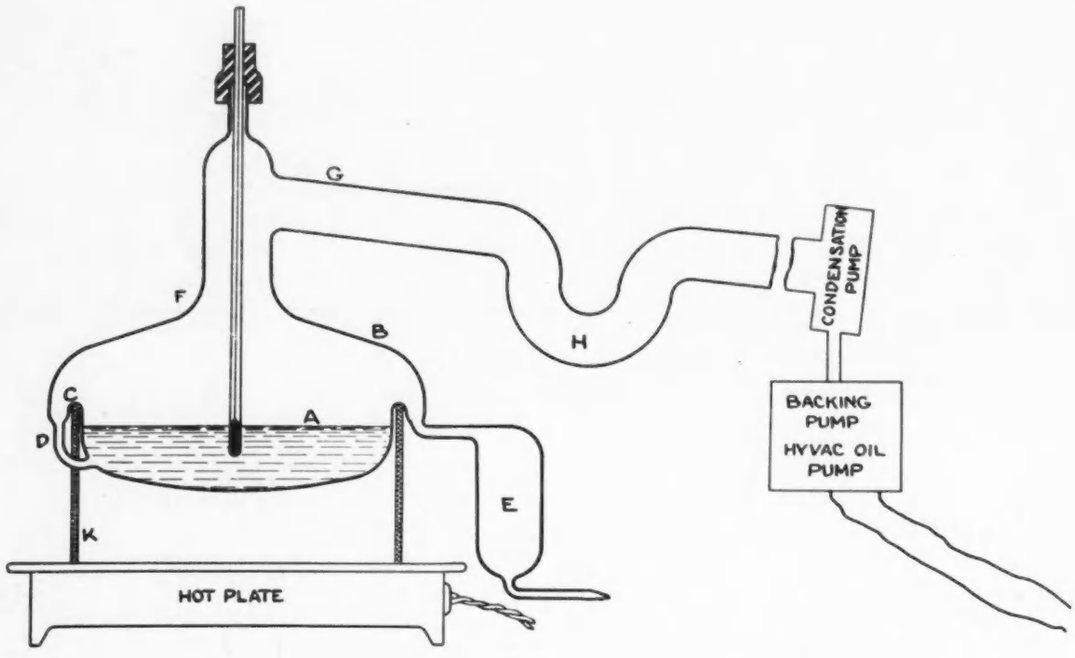

FIG. 1.

dle and then pushed in to yield a flat alembic. The size of flask is limited only by the danger of collapse under vacuum. Three vessels constructed by ourselves from liter flasks all "imploded," and it was found necessary to let a professional glass blower construct a vessel from a flask, the walls of which were previously thickened at the critical places. The two halves A and B may be called the container and the condenser. They are separated by the annulus C. The annulus and the container are connected by a small tube D. Two chambers E are sealed to the annulus at points equidistant from one another and from D. The neck F is pulled off short in a constriction through which a filling funnel and later a thermometer may be pushed. A side tube G, two centimeters in diameter, is provided with a short bend on its way to union with a Langmuir condensation pump.

In use the alembic is filled to a little below the annulus and is supported by a metal collar K on a hot plate. Evacuation is commenced by operating the backing pump until the liquid begins to froth from the evolution of gases or solvent. Generally there is much explosive spurting, which splashes the liquid onto the receiver walls. The whole apparatus is therefore tipped slightly toward D by placing a wedge under the collar K, so that the splashings may return to the container. The receiver walls should now feel slightly warm to the touch, and the spurting should be becoming less frequent. The condensation pump is now turned on and the walls of B carefully inspected for signs of distillation. If this does not occur with the thermometer reading less than 70–100° C. (for castor oil) it means that volatile decomposition products are being liberated at too great a rate for removal by the pumps. The pressure is unable to fall to less than a hundredth of a millimeter, and none of the molecules leaving the surface of the liquid in A are able to reach the condensing wall without collision. The trap H is therefore packed around with solid carbon dioxide in a wrapper of absorbent cotton. Almost immediately distillation will start, without, however, any spurting or signs of

boiling showing in the mother liquor. The alembic is now tipped so that liquid collecting in the annulus falls into one container. When a sufficient fraction has been collected, the angle is altered and a middle fraction taken in the second container. A third portion is left undistilled. When the vacuum has been relieved, the tips of the containers are broken and the fractions withdrawn.

Not every liquid requires this drastic procedure. With all but the most recalcitrant either condenser or condensation pump can be omitted. The following table will serve as guidance.

Backing Pump Only	*Backing Pump and Condensation Pump*
Heavy paraffin hydrocarbons	Dibenzyl malonate
Aromatic esters	Tolyl benzene, etc.
Aromatic acids	Anthracene oils

Backing Pump, Condensation Pump, and Condenser	
Glycerine	Vegetable oils,
Castor oil	essences, and
Fatty glycerides	animal fats

The flat sublimation still of Fig. 1 is suitable for the most difficult substances, but it is not the most convenient form of apparatus for the preparation of small pure samples of substances of more stable character. For such cases we use the electrically warmed alembic shown in the photograph of Fig. 2.

The retort is a 4″ length of pyrex tubing, 1½″ in diameter, terminating in a re-entrant flask. Two receivers and a return tube take care of the distillate. The heating is secured by winding about two meters of nichrome wire (10 ω per meter) over a core of asbestos paper, and covering the winding with two or three layers more paper. The current is supplied from the house main through an adjustable resistance.

In all very high vacuum distillations it is a great help to give the material a preliminary exhaustion. It is placed in a flask with a rubber stopper accommodating a wide glass tube which passes over into another flask. A second tube from this second flask passes to the oil pump. The first flask is stood in a basin of warm water, and the second flask is allowed to remain cool (or is placed in ice and salt). An ordinary mercury U-tube manometer may be included in the train. After an hour or two the manometer is found to register less than one millimeter difference of pressure, and the substance may be considered free enough from volatile impurities for rapid purification in the sublimation still.

Fig. 2.

Electrically heated still for small samples.

Organic Chemicals as Analytical Reagents

VIII REAGENTS FOR ALUMINUM

ALIZARIN S

Atack, J. S. Chem. Ind. *34*, 937 (1915)

This reagent will detect 1 part of aluminum in ten million parts of water, providing that only small amounts of other metals are present. About 1 cc. of a 0.1% filtered solution of alizarin S is added to 5 cc. of the neutral solution to be examined. Ammonia is added slowly until a purple coloration is obtained. The solution is then boiled for a few minutes and allowed to cool. A red color or precipitate remaining after acidifying with cold dilute acetic acid, indicates the presence of aluminum.

AURIN TRICARBOXYLIC ACID (Ammonium Salt)

Yoe and Hill, J. A. C. S. *49*, 2395 (1927)

About 300 cc. of a sample of potable water is treated with hydrochloric acid, evaporated to dryness, and ignited. After taking up with a small amount of hydrochloric acid, the silica is filtered off. After dilution, the iron and aluminum are precipitated by means of ammonium hydroxide, and the aluminum separated by treatment with nitric acid and sodium hydroxide. To the neutralized solution hydrochloric acid and ammonium acetate are added, and then a 0.1% solution of the reagent. Ammonium hydroxide and ammonium carbonate solutions are added and the color of the resulting solution compared in a Nessler tube against known standards. The method will detect 1 part of aluminum in 25 million of water.

HEMATOXYLIN

Hatfield, Ind. & Eng. Chem. *16*, 233 (1924)

This reagent is recommended for determining soluble aluminum in filtered waters. To a Nessler tube containing 50 cc. of the water to be tested are added 1 cc. of saturated ammonium carbonate and 1 cc. of a 0.1% hematoxylin solution. After mixing and standing for 15 minutes, 1 cc. of 30% acetic acid is added. The resulting yellow color is compared with standards containing from 0 to 1 p.p.m. aluminum which have been treated in the same manner.

O-HYDROXYQUINOLINE

Kolthoff and Sandell, J. A. C. S. *50*, 1900 (1928)

Aluminum is precipitated quantitatively by this reagent from dilute acetic acid solutions containing ammonium acetate. By this method aluminum may be separated from beryllium, which is not precipitated under these conditions. A 5% solution of the reagent in 2N acetic acid is added in excess to the warm, slightly acid aluminum solution. An excess of 2N ammonium acetate is slowly added, precipitating the aluminum compound. After filtering, washing with cold water, and drying at 120° the precipitate contains 11.10% Al_2O_3.

New Chemicals

The following preparations have been added to our list since the last issue of this bulletin:

*Acetyl p-Toluidine (Pract.)
*1-Amino-2-Naphthol-4-Sulfonic Acid
*2-Bromooctane
*2-Chlorophenyl-4-toluenesulfonate
*4-Chlorophenyl-4-toluenesulfonate
*2.4-Dichlorophenyl-3.4-dichlorobenzenesulfonate
*2.4-Dichlorophenyl-4-toluenesulfonate
*Diethylene Glycol Monoethyl Ether (Pract.)
*3-Methyl-4-chlorophenyl-4-toluenesulfonate
*Methyl Nitrate
*Phenyl-4-chlorobenzenesulfonate
*Phenyl-3.4-dichlorobenzenesulfonate

Organic Chemicals as Analytical Reagents

VI REAGENTS FOR IRON

CUPFERRON

Baudisch and King, Ind. and Eng. Chem. *3*, 629 (1911)

Iron and copper are precipitated from acid solutions by this reagent. By washing the precipitate with dilute ammonia the copper compound dissolves, leaving the insoluble iron salt on the filter. The sample is dissolved in concentrated hydrochloric acid, oxidized with potassium chlorate and, after expelling the chlorine, diluted with distilled water. The reagent (3 gm. of cupferron in 50 cc. water) is added with stirring, giving a brownish red precipitate. A white crystalline precipitate appears when all of the iron is out of the solution. After washing with water and dilute ammonia the precipitate is ignited and weighed as Fe_2O_3.

DIMETHYLGLYOXIME

Tschugaeff and Orelkin, Z. Anorg. Chemie. *89*, 401 (1914)

A solution containing ferrous-iron is colored a deep red when a solution of dimethylglyoxime is added. Ferric-iron, which does not give the test, can be easily reduced quantitatively by hydrazine sulfate. Fifty cc. of the solution to be examined is treated with 1 gm. of hydrazine sulfate and 5 cc. of a saturated alcoholic dimethylglyoxime solution and then heated to boiling. Twenty-five cc. of 25% ammonia is then added, continuing the boiling for 0.5 minute. After cooling, it is diluted to 100 cc. and compared in a colorimeter with a standard iron solution similarly treated.

ISO-NITROSOACETOPHENONE

F. Krohnke in Berichte, *60*, 527 (1927)

This reagent is employed in the form of a decinormal solution in chloroform. The dilute, neutral solution of ferrous salt is treated with 1 cc. of the reagent and 1 cc. of decinormal ammonia. As little as 0.03 mg. of ferrous iron per liter gives a blue chloroform layer.

ACETYLACETONE

Pulsifer, J. A. C. S., *26*, 967 (1904)

Three-millionths of a gram of iron in 50 cc. of water will give a distinct red color when treated with a ½% solution of acetylacetone. The depth of color in such solutions is proportional to the amount of iron present, within the limits of 0.000003 g. to 0.0006 g. Most of the other inorganic salts cause no interference even in amounts as large as 0.2 gram.

SALICYLIC ACID

Gregory, J. C. S., *93*, 93 (1908)

Salicylic acid gives a violet coloration to iron solutions, changing to a deep red when sodium acetate is added. To the ferric-iron solution 20 cc. of a concentrated sodium acetate solution is added and then 10 cc. of 2% salicylic acid in glacial acetic acid. If copper is present, the green color may be removed by the addition of a few drops of 3% potassium cyanide. The solution is diluted up to a definite volume and the red color compared with that of a known iron solution which has had the same treatment.

New Chemicals

The following preparations have become available during the summer.

*Acetyl Piperidine (Pract.)
*n-Amyl Acetate
*n-Amyl n-Butyrate
*n-Amyl Propionate
*Bromopicrin
*Carvoxime
*Cysteine Hydrochloride
*α-β-Dibromoethylene
*p.p′-Dihydroxydiphenyl
Ethylene glycol Monomethyl Ether (Pract.)
Magnesium Perchlorate (Anhydrous)

**Made or purified in the Kodak Research Laboratories.*